A POSSIBLE REPRESENTATION OF A VIRIAL STATE EQUATION IN THE FORM OF A FINITE PRESSURE POLYNOMIAL

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It is shown that the transition from a virial state equation with a finite number of terms to an equation in the form of a polynomial in powers of pressure by using known recalculation formulas is impossible, without losing accuracy in describing the initial p, ρ, T data array. Formulas are proposed to estimate the error associated with such a transition.

Among different thermal state equations for a real gas, of special importance is the virial equation

$$Z = 1 + B\rho + C\rho^2 + D\rho^3 + E\rho^4 + ..., \qquad (1)$$

where $Z = p/\rho RT$ is the compressibility (or nonideality) factor. The RHS of (1) is an infinite series in terms of powers of density. The coefficients B, C, D, etc. of this power series are temperature functions and are, correspondingly, called the second (SVC), third (TVC), etc. virial coefficients. According to (1) the virial coefficients can be determined by using the limit relations

$$B = \lim_{\rho \to 0} \left(\frac{\partial Z}{\partial \rho} \right)_T ,$$

$$C = \frac{1}{2} \lim_{\rho \to 0} \left(\frac{\partial^2 Z}{\partial \rho^2} \right)_T , \qquad (2)$$

$$D = \frac{1}{6} \lim_{\rho \to 0} \left(\frac{\partial^3 Z}{\partial \rho^3} \right)_T , \text{ etc.}$$

The advantages and disadvantages of the virial state equation are sufficiently detailed in the literature (see, e.g., [1]). Let us emphasize only its main advantage, noting that the virial equation is grounded theoretically and reflects the relationship between the microscopic parameters of a gas system and its macroparameters p, ρ, and T. So, the SVC is bound up with the Z − 1 deviations from the ideal gas behavior due to the pair interaction of molecules; the TVC, due to the triple interaction of molecules, etc. In principle, the virial coefficients can be calculated by statistical physics methods if the gas molecule interaction potential is known. In addition, the virial coefficients can be obtained from sufficiently exact experimental p, ρ, T data by using the limit relations

$$B = \lim_{\rho \to 0} \frac{Z - 1}{\rho} ,$$

$$C = \lim_{\rho \to 0} \left(\frac{Z - 1}{\rho^2} - \frac{B}{\rho} \right) , \qquad (3)$$

$$D = \lim_{\rho \to 0} \left(\frac{Z - 1}{\rho^3} - \frac{B}{\rho^2} - \frac{C}{\rho} \right) , \text{ etc.}$$

Relations (3) and (2) are equivalent. The virial coefficients found by relations (3) can be called true virial coefficients.

In practice, sufficiently reliable values of the virial coefficients cannot be obtained by relations (3) since with decreasing density and, hence, pressure the relative error in their determination grows. As a rule, the virial coefficients are determined not at a point $\rho \to 0$ but by using approximations of the experimental p, ρ, T data over a finite pressure range.

In practice, especially when the properties of gas mixtures are being studied and calculated, more often the equation

$$Z = 1 + B'p + C'p^2 + D'p^3 + E'p^4 + ..., \tag{4}$$

is used, whose RHS is an infinite series in terms of powers of pressure, and the coefficients B', C', D', etc. of this series are functions of temperature as well and are determined by the limit relations

$$B' = \lim_{p \to 0} \left(\frac{\partial Z}{\partial p} \right)_T,$$

$$C' = \frac{1}{2} \lim_{p \to 0} \left(\frac{\partial^2 Z}{\partial p^2} \right)_T, \tag{5}$$

$$D' = \frac{1}{6} \lim_{p \to 0} \left(\frac{\partial^3 Z}{\partial p^3} \right)_T, \text{ etc.,}$$

similar to relations (2). However, these coefficients are lacking the physical meaning which is peculiar to the virial coefficients of equation (1). The virial coefficients and the coefficients of equation (4) are connected by relations called transition formulas. These formulas can be obtained in two ways: algebraically and by limit relations (2) and (5).

Upon solving equation (1) with respect to pressure:

$$p = RT\,(\rho + B\rho^2 + C\rho^3 + D\rho^4 + E\rho^5 + ...) \tag{6}$$

and upon substituting the obtained result into Eq. (4) we obtain an infinite power series in density in the RHS of (4). Upon equating the coefficients of this series to the virial coefficients of series (1) under the same powers of density we obtain the following transition formulas:

$$B' = B/RT,$$

$$C' = (C - B^2)/R^2T^2,$$

$$D' = (D - 3CB + 2B^3)/R^3T^3, \tag{7}$$

$$E' = (E - 4DB - 2C^2 + 10CB^2 - 5B^4)/R^4T^4, \text{ etc.}$$

These very formulas can be derived by replacing the differentiation variable in limit relations (2):

$$\lim_{\rho \to 0} \left(\frac{\partial Z}{\partial \rho} \right)_T = \lim_{\rho \to 0} \left(\frac{\partial Z}{\partial p} \cdot \frac{\partial p}{\partial \rho} \right)_T,$$

$$\lim_{\rho \to 0} \left(\frac{\partial^2 Z}{\partial \rho^2} \right)_T = \lim_{\rho \to 0} \left(\frac{\partial Z}{\partial p} \frac{\partial^2 p}{\partial \rho^2} + \frac{\partial^2 Z}{\partial p^2} \left(\frac{\partial p}{\partial \rho} \right)^2 \right)_T,$$

$$\lim_{\rho \to 0} \left(\frac{\partial^3 Z}{\partial \rho^3} \right)_T = \lim_{\rho \to 0} \left(\frac{\partial Z}{\partial p} \frac{\partial^3 p}{\partial \rho^3} + 3 \frac{\partial^2 Z}{\partial p^2} \frac{\partial^2 p}{\partial \rho^2} \frac{\partial p}{\partial \rho} + \frac{\partial^3 Z}{\partial p^3} \left(\frac{\partial p}{\partial \rho} \right)^3 \right)_T, \tag{8}$$

$$\lim_{\rho \to 0} \left(\frac{\partial^4 Z}{\partial \rho^4} \right)_T = \lim_{\rho \to 0} \left(\frac{\partial Z}{\partial p} \frac{\partial^4 p}{\partial \rho^4} + 4 \frac{\partial^2 Z}{\partial p^2} \frac{\partial^3 p}{\partial \rho^3} \frac{\partial p}{\partial \rho} + \right.$$

$$\left. + 3 \frac{\partial^2 Z}{\partial p^2} \left(\frac{\partial^2 p}{\partial \rho^2} \right)^2 + 6 \frac{\partial^3 Z}{\partial p^3} \frac{\partial^2 p}{\partial \rho^2} \left(\frac{\partial p}{\partial \rho} \right)^2 + \frac{\partial^4 Z}{\partial p^4} \left(\frac{\partial p}{\partial \rho} \right)^4 \right)_T, \text{ etc.}$$

As follows from equation (6) we have

$$\lim_{\rho \to 0} p = 0,$$

$$\lim_{\rho \to 0} \left(\frac{\partial p}{\partial \rho} \right)_T = RT,$$

$$\lim_{\rho \to 0} \left(\frac{\partial^2 p}{\partial \rho^2} \right)_T = 2RTB,$$

$$\lim_{\rho \to 0} \left(\frac{\partial^3 p}{\partial \rho^3} \right)_T = 6RTC, \tag{9}$$

$$\lim_{\rho \to 0} \left(\frac{\partial^4 p}{\partial \rho^4} \right)_T = 24RTD, \text{ etc.}$$

When substituting these limits into equation (8) with regard for (2) and (5), we obtain formulas (7).

It should be noted that formulas (7) in accord with their derivation are valid only for the infinite series and for the true virial coefficients obtained by limit relations (3) and similar to the pressure power series coefficients. In practice, we are dealing both with finite polynomials since the virial series in (1) at moderate densities converges sufficiently rapidly and with coefficients obtained by approximating the experimental p, ρ, T data over some parameter range. Therefore, use of formulas (7), when going from the density power polynomial to the pressure power one while keeping the same number of terms, results in the accuracy in determining the initial data being much reduced.

Despite the fact that the above distinctive feature of the transition formulas is well known, in different articles and even in textbooks the authors go from the density power polynomial to the pressure one, keeping in the last one the same number of terms while not analyzing the accuracy of the equation obtained. Let us try to find out what extra error arises in such manipulations.

Based on formulas (7), let us go from the virial equation with the second virial coefficient alone

$$Z = 1 + B\rho, \tag{10}$$

valid at small densities, to the equation in terms of variables T and p:

$$Z_p = 1 + \frac{B}{RT}\, p, \tag{11}$$

and upon directly transforming equation (10) we obtain the equation

$$Z = 1 + \frac{B}{RT\,(1 + B\rho)}\, p. \tag{12}$$

equivalent to it. Comparison of (11) and (12) shows that equations (10) and (11) will be equivalent only at $B\rho \to 0$. Otherwise, the error in describing the p, ρ, T data by equation (11) grows as the term $B\rho$ increases.

It is well known that over a sufficiently wide parameter range experimental p, ρ, T data can be described by two virial coefficients

$$Z = 1 + B\rho + C\rho^2. \tag{13}$$

Using formulas (7) and assuming the highest virial coefficient equal to zero starting with the fourth one, we arrive at the equation

$$Z_p = 1 + \frac{B}{RT}\, p + \frac{C - B^2}{R^2 T^2}\, p^2 + \frac{2B^3 - 3BC}{R^3 T^3}\, p^3 + \frac{10B^2 C - 5B^4 - 2C^2}{R^4 T^4}\, p^4 + \ldots \tag{14}$$

with an infinite power series in the RHS. This series converges, at least, over the parameter range where equation (13) is valid, but as a check has shown it converges slowly.

As is known, the remainder r_n of series (14) is an absolute error

$$\Delta Z_p^{(n)} = Z\,(\rho,\ T) - Z_p^{(n)}, \tag{15}$$

which is additionally included when going from equation (13) to equation (14) with the n first terms.

To go from Eq. (13) to (14) with a pressure polynomial equivalent from the viewpoint of the description of the p, ρ, T data, it is necessary that the remainder r_n be less at least by an order of magnitude than the accuracy with which equation (14) describes these p, ρ, T data.

Series (14) incorporating both positive and negative terms with a very complex procedure to construct its coefficients does not allow its remainders to be analyzed directly. Let us consider the method of estimating the remainders of series (14), meaning the transformation of Eq. (13) to a mixed polynomial containing the first n terms of (14) with powers of p and a finite number of terms with powers of ρ, starting with the n-th power.

Let us write down some extra formulas obtained by simple but rather tedious transformations of equation (13):

$$\rho = \frac{p}{RT} - B\rho^2 - C\rho^3,$$

$$\rho^2 = \frac{p^2}{R^2 T^2} - 2B\rho^3 - (B^2 + 2C)\,\rho^4 - 2BC\rho^5 - C^2\rho^6,$$

$$\rho^3 = \frac{p^3}{R^3T^3} - 3B\rho^4 - 3(B^2 + C)\rho^5 - B(B^2 + 6C)\rho^6 -$$

$$- 3C(B^2 + C)\rho^7 - 3BC^2\rho^8 - C^3\rho^9 \quad , \text{etc.} \tag{16}$$

Substituting powers of density from formulas (16) into equation (13) yields, upon grouping the terms, new equations equivalent to equation (13):

$$Z = 1 + \frac{B}{RT} p + \frac{C - B^2}{R^2T^2} p^2 + \Delta Z_p^{(3)},$$

$$Z = 1 + \frac{B}{RT} p + \frac{C - B^2}{R^2T^2} p^2 + \frac{2B^3 - 3BC}{R^3T^3} p^3 + \Delta Z_p^{(4)} \quad , \text{etc.,} \tag{17}$$

where

$$\Delta Z_p^{(3)} = -BC\rho^3 - (C - B^2)\rho^2(Z^2 - 1),$$

$$\Delta Z_p^{(4)} = -BC\rho^3(1 - Z^3) - (C - B^2)\rho^2(Z^2 - 1 - 2Z^3B\rho) \quad , \text{etc.,} \tag{18}$$

are convenient for analyzing the extra errors in $\Delta Z^{(n)}_p$. Note that constructing the polynomial in powers of pressure in this manner, we go from equation (13) to equation (14) irrespective of what the coefficients B and C mean in Eq. (13): true coefficients are the virial coefficients or those obtained by approximating experimental p, ρ, T data over some state parameter range.

As is seen from the first equations of (17) and (18), the transition from Eq. (13) to the equation

$$Z_p^{(3)} = 1 + \frac{B}{RT} p + \frac{C - B^2}{R^2T^2} p^2 \tag{19}$$

involves a substantial error growth. As terms with higher powers of pressures (the second equations of (17) and (18)) are included in the polynomial $Z^{(n)}_p$, the error $\Delta Z^{(n)}_p$ decreases.

To check the analytical results on a particular substance we used standard reference data (SRD) [2] on the thermal properties of nitrogen over the range of temperatures 180-400 K and of pressures 0.1-10 MPa, where, e.g., the thermodynamic properties of humid gases are of practical interest.

The initial data array included 143 points (13 isotherms) and was described by virial state equation of form (13):

$$Z = 1 + (b_0 + b_1/T + b_2/T^2 + b_4/T^4)\rho + (c_0 + c_2/T^2)\rho^2, \tag{20}$$

where the density is measured in mole/cm^3 and the temperature in K. The numerical values of the coefficients included in (20) are determined by the least-square method:

$$b_0 = 42,4924; \quad b_4 = 3,03941 \cdot 10^9;$$

$$b_1 = -10792,8; \quad c_0 = 1267,68;$$

$$b_2 = -1,07310 \cdot 10^6; \quad c_2 = 3,09358 \cdot 10^7.$$

Equation (20) describes the initial data array with a mean square error $\sigma = 0.017\%$. The maximum error is 0.064% at T = 180 K and p = 2 MPa. Figure 1 illustrates the histogram of the deviations of the values of Z

$$\delta Z = (Z - Z_{[2]})/Z_{[2]} \tag{21}$$

calculated by Eq. (20) from the data of [2]. The histogram is useful in the visualization of the trend in the qualitative and quantitative aspects of the approximation of the initial nitrogen p, ρ, T data array.

When going from Eq. (20)-(19) in terms of the independent variables p and T, one is able to determine how the approximation accuracy of the initial data array gets worse. The calculations have shown that deviations δZ_p not exceeding ~0.1% are observed on the isotherms T $\geq$ 300 K where the value of the density is $\rho \leq 0.35\rho_{cr}$. As the temperature decreases and the pressure (density) increases the discrepancies start to sharply increase and attain a maximum value $\delta Z_p = -9.7\%$ at T = 180 K and p = 10 MPa.
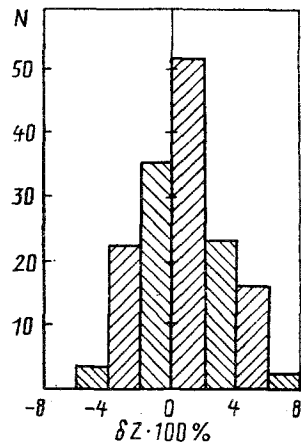
Fig. 1. Histogram of the deviations of the values of Z
calculated by Eq. (20) from data [2].

TABLE 1. Deviations of the Values of the Nitrogen Compressibility Factor
According to Data [2] Calculated by Equations (20) and (19) Expressed
in % and in Absolute Values on The 10 MPa Isobar

T, K	$\rho \cdot 10^3 \dfrac{mole}{cm^3}$	$\omega = \dfrac{\rho}{\rho_{cr}^{*)}}$	δZ, %, (20)	δZ_p, %, (19)	$Z_{[2]} - Z_p^{(3)}$	$\Delta Z_p^{(3)}$ (18)
180	8,887	0,7951	—0,027	—9,70	0,0729	0,0726
200	7,123	0,6373	0,000	—4,42	0,0373	0,0373
220	6,049	0,5412	0,011	—2,13	0,0192	0,0193
240	5,311	0,4752	0,021	—1,02	0,0096	0,0098
260	4,763	0,4261	0,010	—0,46	0,0045	0,0046
280	4,334	0,3878	0,000	—0,17	0,0017	0,0018
300	3,989	0,3569	0,060	0,03	—0,0003	0,0003
320	3,699	0,3309	0,020	0,08	—0,0008	—0,0006
340	3,454	0,3090	0,020	0,12	—0,0012	—0,0010
360	3,244	0,2902	0,019	0,13	—0,0013	—0,0012
380	3,058	0,2736	—0,029	0,09	—0,0009	—0,0013
400	2,897	0,2592	0,010	0,13	—0,0013	—0,0012
420	2,751	0,2461	—0,029	0,08	—0,0008	—0,0011

*The value of the critical density is taken from [2]: $\rho_{cr} = 0.011177$
mole/cm³.

The dynamics of the growth of the deviations δZ_p with the coefficients calculated by formulas (7) as against δZ of (21) are cited in Table 1 (10 MPa isobar). The last column of this table contains the values of $\Delta Z^{(3)}_p$ calculated by formula (18). It is seen that these values are equal to the excess of the approximation error by equation (19), whose coefficients are obtained by formulas (7) (last column).

Including the fourth expansion term in the state equation for Z_p decreases the approximation error of the initial data array by the values determined by the second equation of (18).

Thus, this study enables one to conclude the following.

1. If the initial p, ρ, T data array is described by the virial coefficient with the experimental error, then we cannot go to the pressure expansion equation by known formulas (7) with the same number of terms, not losing a substantial error or not greatly decreasing the parameter range over which these data are given.

2. From the virial state equation with the second polynomial in powers of density, when formulas (7) are used, we obtain Eq. (14) with an infinite pressure power series with a relatively weak convergence. All coefficients of this series are combinations of the virial coefficients B and C.

3. When going from the virial state equation to equation (14) with a fixed number of pressure power terms, we must use the expressions for the remainders $\Delta Z^{(n)}_p$ of (18) to reveal the necessary number of pressure power terms in (14) in order to provide the assigned accuracy in describing the initial data or to set a limit on the parameter range over which these data are given.

LITERATURE CITED

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